学校编码：10384　　分类号_____密级_____
学号：20620110153662　　UDC_____

厦门大学

博 士 学 位 论 文

聚芳醚砜类膜的制备、表征及分离甲醇/甲基叔丁基醚

Poly (aryl ether sulfone) Membranes: Preparation, Characterization and Application in Separating MeOH/MTBE Mixtures

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论文提交日期：　年　月
论文答辩时间：　年　月
学位授予日期：　年　月

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摘 要

甲基叔丁基醚 (MTBE) 是一种优良的汽油高辛烷值添加剂和抗爆剂，在精细化工领域也有广泛的应用。MTBE 由甲醇(MeOH)和异丁烯反应制得。在反应过程中，往往需要添加过量的 MeOH(大于 20 wt%)以提高反应转化率。因此，需将过剩的 MeOH 从产品中分离出来。但传统分离方法能耗大，工序复杂。渗透汽化(PV)技术作为一种低能耗、分离效率高、过程简单的新型膜分离技术，为上述问题的解决提供了一种新途径。渗透汽化技术的核心为膜材料。本论文应用聚芳醚砜类材料(酚酞侧基聚芳醚砜(PES-C)及其改性膜和合成的 PES 嵌段聚合物)制备渗透汽化膜，用于分离 MeOH/MTBE 体系。利用 X-射线衍射(XRD)、红外光谱(FTIR)、扫描电镜(SEM)、透射电镜(TEM)、热重分析(TGA)、正电子湮灭(PALS)和水接触角测试等手段对膜的物化性质和微观结构进行表征，讨论了上述表征结果和膜分离性能之间的关系。

制备了 PES-C 膜，考察了溶剂种类、退火时间和退火温度对膜分离性能的影响。PALS 表征结果证明 PES-C 膜的空穴直径(0.51 nm)处于 MeOH 分子动力学直径(0.40 nm)和 MTBE 分子动力学直径(0.62 nm)之间，所以 PES-C 膜的分离因子较高。但由于 PES-C 优良的抗溶剂性能，通量较小。

为提高 PES-C 膜的渗透通量，且分离因子牺牲最小，采用与聚乙烯吡咯烷酮(PVP)共混和在 PES-C 中引入磺酸基团两种方法对 PES-C 膜进行改性。对 PES-C/PVP 共混膜的表征证明两者相容性好。随 PVP 含量的增加，共混膜的自由体积分数和空穴直径增大，渗透通量也一直增大，而 PVP 含量为 16wt%时，分离因子出现最大值(889)。对于 SPES-C 膜，引入磺酸基团有效地改善了膜的亲水性，通过控制磺化度可调节 SPES-C 的亲憎水平衡。TEM 表征结果证明磺酸基团相互作用形成团簇，进而形成离子传输通道。分离性能测试结果表明膜的通量随磺化度增加而升高，分离因子在磺化度为 0.64 时达到最大值(1300)。

与共混比较，引入磺酸基团对提高 PES-C 分离性能的效果更好。因此，为进一步提高 SPES-C 膜的通量，在其中引入聚乙烯亚胺(PEI)制备了均质聚电解质膜。SEM 结果表明两者相容性好。PEI 的引入降低了膜的结晶度。另外，SPES-C 和 PEI 之间有离子交联结构存在。分离性能测试结果表明随着 PEI 含量的增加，聚电解质膜的渗透通量不断升高。当 PEI 含量为 16wt%，分离因子最大(1860)。

合成了$[Cu_2(bdc)_2(bpy)]_n$并将其成功引入到SPES-C中制备了SPES-C/$[Cu_2(bdc)_2(bpy)]_n$杂化膜。与MTBE相比，$[Cu_2(bdc)_2(bpy)]_n$优先吸附MeOH分子，将其引入SPES-C中有望提高其分离性能。随$[Cu_2(bdc)_2(bpy)]_n$添加量的增加，杂化膜的渗透通量和分离因子同时增加。当$[Cu_2(bdc)_2(bpy)]_n$含量为20wt%时，渗透通量和分离因子分别为0.288 $kg\cdot m^{-2}\cdot h^{-1}$ 和1870。

调节膜的自由体积参数和构建离子传输通道是制备分离性能优良的PES膜的关键。因此，制备了含芴的PES嵌段聚合物。芴使亲水段呈螺旋状，利于调节膜的自由体积参数，另外亲水段与憎水段的微相分离利于构筑离子传输通道。PALS和小角X射线散射(SAXRD)表征结果证明上述设想是成立的。分离性能测试结果表明PES-x31y9膜的通量最高，达到0.334 $kg\cdot m^{-2}\cdot h^{-1}$，渗透侧MeOH含量仍高于98wt%。

关键词：渗透汽化；聚芳醚砜；MeOH/MTBE体系

Abstract

Methyl *tert*-butyl ether (MTBE) is an excellent gasoline octane number enhancer and anti-knocking agent. It is also widely used in fine chemical industry. MTBE is produced by the reaction of methanol (MeOH) and isobutylene, in which excessive up to 20 wt% MeOH is added into the reactor to increase the conversion rate. This will encounter a difficulty in purification. However, the conventional process is energy intensive and complex. Pervaporation (PV), as a new membrane technology with features of low energy consumption, efficient and simple, provides an alternative for solving the problem mentioned above. The core of PV is the membrane material. In this dissertation, polyarylethersulfones (PESs) including polyarylethersulfone with cardo (PES-C) and modified PES-C as well as synthesized PES multiblock copolymer were used to prepare membranes for PV separation of MeOH/MTBE mixture. XRD, FTIR, SEM, TEM, TGA, PALS and water contact angle measurement were applied to characterize the phisico-chemical properties and microstructure of the as-prepared membranes. And the relationship between membrane structure and performance was discussed thoroughly.

PES-C membranes were prepared. The effect of solvent, annealing time and annealing temperature on the performance was investigated. The result of PALS showed that the diameter of the cavity in PES-C membrane (0.51 nm) lay between the molecule dynamic diameter of MeOH (0.40 nm) and MTBE (0.62 nm), which was responsible for its high separation factor. But the permeation flux was low due to its excellent solvent resistance.

In order to enhance the permeation flux of PES-C membrane without remarkblely sacrificing its separation factor, PES-C was modified by blending with PVP or/and introducing sulfonic acid group. For PES-C/PVP blending membrane, good compatibility between the two polymers was confirmed. With increasing PVP content, the fractional free volume and the diameter of the cavity increased leading to

the enhancement of permeation flux. When the mass fraction of PVP was 16%, the separation factor reached to the maximum of 889. The hydrophilicity of SPES-C membrane was improved by introducing sulfonic acid group. And the hydrophilic-hydrophobic balance of the membranes can be realized by controlling the sulfonation degree (SD). TEM results indicate that sulfonic acid groups interact with each other to form $–SO_3H$ clusters that can further construct the so-called transport channel. The performance testing results showed that the permeation flux increased with increasing SD. The maximum separation factor of 1300 was achieved when SD was 0.64.

Comparing with blending method, the effect of introducing $–SO_3H$ group wins. In order to improve the permeation flux of SPES-C membrane, polyethleneimine (PEI) was applied to prepare homogeneous SPES-C/PEI polyelectrolyte membrane. SEM results showed that the compatibility was good. PEI reduced the crystalline of the membranes. In addition, there exists ionic complexation between the two polyelectrolytes. With increasing PEI content, the permeation flux increased. When the mass fraction of PEI was 16%, the separation was the highest value of 1860.

$[Cu_2(bdc)_2(bpy)]_n$ was also synthesized and incorporated into SPES-C matrix to prepare SPES-C/$[Cu_2(bdc)_2(bpy)]_n$ mixed matrix membranes. $[Cu_2(bdc)_2(bpy)]_n$ adsorbed MeOH over MTBE, which contributed to the enhancement of separation performance. By increasing $[Cu_2(bdc)_2(bpy)]_n$ loading, the permeation flux and separation factor increased simultaneously. The permeation flux and separation factor reached 0.288 $kg \cdot m^{-2} \cdot h^{-1}$ and 1870 respectively at 20 wt% $[Cu_2(bdc)_2(bpy)]_n$ loading.

In general, tailoring the free volume parameters and constructing the transport channel are the critical issues for improving the separation performance of PES membranes. We synthesized fluorene-containg PES multiblock copolymer. The introduction of fluorene makes the hydrophilic segment helical structure, which is beneficial to adjust the free volume parameters. What is more, the microphase separation between hydrophilic and hydrophobic segment can construct the transport channel. PALS and SAXRD results verified above hypothesises. PES-x31y9 membrane has the highest permeation flux of 0.334 $kg \cdot m^{-2} \cdot h^{-1}$. Although its

separation factor is as low as 287, the mass fraction of MeOH in the permeate was still higher than 98 wt%.

Key words: Pervaporation; Polyarylethersulfone; MeOH/MTBE mixture

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